



Push–Pull Systems

Stimuli-Responsive Organic Dyes with Tropylium Chromophore

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Abstract: Tropylium ions possess an interesting combination of structural stability and chemical reactivity due to its Hückel aromaticity and its positively charged polyene nature, respectively. Herein we exploit the chemical versatility and unique structural properties of the tropylium ion to derive a family of novel push–pull organic dyes with strong absorption in the visible range via simple and practical synthetic protocols. These stable organic dyes are highly stimuli-responsive, as demonstrated by their sensitivity towards solvent, pH change, redox reaction, Lewis base and counterion, which marks them as potentially useful compounds for opto-electronic applications.

Synthetic organic dyes have been used in a wide range of applications such as dye-sensitized solar cells (DSSCs),^[1] organic light-emitting diodes (OLEDs),^[2] catalytic chemistry,^[3] sensors,^[4] and bio-imaging.^[5] Push-pull or donor-acceptor organic dyes are of particular interest for opto-electronic applications.^[6] Cationic dyes, a sub-class of donor-acceptor organic dyes, have attracted significant attention due to their versatile and tunable physicochemical properties.^[6b,7] These compounds generally have superior solubility in aqueous media in comparison to the neutral analogues. Another useful feature is that solvents and counterions often have immense effects on photoactivities of cationic dyes.

A diverse family of cationic moieties have been investigated as chromophores in synthetic organic dyes, ranging from xanthene and polymethine frameworks such as rhodamines^[8] and cyanines^[9] to structurally simpler building blocks such as triarylcarbenium,^[10] triangulenium^[11] and helicenium ions.^[11d,12] Chemical installation of these electron-poor chromophores to electron-rich frameworks, either directly or through an extended conjugated bridge, gives access to an enormous pool of valuable push–pull molecules for various applications.^[11d] Despite being discovered as the first stable carbocation,^[13] the non-benzenoid aromatic tropylium ion^[14] has been rarely used as electron acceptors in synthetic organic dyes,^[15] except for a number of examples with the related azulenium^[16] and tropolonate^[17] scaffolds or Perovskite-type tropylium hybrid materials.^[18] The Yamaguchi group recently reported two elegant

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studies employing a fused dithienotropylium system as the polymethine building block for organic dyes with interesting physicochemical properties.^[19]

The tropylium ion possesses a conjugated planar sevenmembered carbocyclic system with 6π electrons and a fully delocalized positive charge. It fulfils Hückel's rule of aromaticity^[20] and enjoys an interesting balance of stability and reactivity.^[21] The Lambert group^[14a] and our group^[22] have recently demonstrated the versatile chemistry of tropylium ion where this carbocation can act as a Lewis acid,^[22a] an electrophile^[22b-d,23] or an oxidant.^[14a,24] Herein, we exploit these chemical reactivities to develop a convenient and practical protocol (Scheme 1) to access a family of tropylium organic dyes with strong absorption in the visible range. The inherent electronic properties of the tropylium moiety on these push-pull dyes renders them highly Bronsted/Lewis base-sensitive, redox-responsive and counterion-sensitive such that they can potentially be useful for a range of applications.

We started our investigation by exploring the installation of the tropylium moiety on electron-rich aromatic systems, namely anilines (see the Supporting Information for the synthesis of indole analogues^[25]), to construct the donor-acceptor motif. The synthesis of organic dyes **4** (Scheme 1) was conven-



Scheme 1. Synthesis of a new family of tropylium-derived organic dyes.

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iently carried out by mixing anilines 1 with two equivalents of tropylium tetrafluoroborate (2) in acetonitrile at room temperature. These reactions proceeded in a step-wise manner through a chemoselective^[26] electrophilic aromatic substitution reaction with the first equivalent of tropylium (Trop) salt followed by an oxidative hydride abstraction^[14a, 24a] with the second equivalent of tropylium.^[25] By controlling the reaction conditions and the amount of tropylium reagent added, we could also stop the reaction at the first step and isolate cycloheptatrienyl (CHT) intermediates 3.^[25] In addition to the scalable protocol and mild reaction conditions,^[25] products 3 or 4 were generally obtained in high to excellent yields.^[25] The rapid formation of these organic dyes and analogues from electron-rich arenes and tropylium salt 2 can be exploited in a simple visualization test for electron-rich arenes (see Supporting Information page S61).^[25]

Organic dyes **4** are water-soluble and stable in aqueous solutions for extended periods of time.^[25] As can be seen from Scheme 1, these organic dyes exhibit strong absorptions in the 540–580 nm region. Organic dyes **4** exhibit interesting solvato-chromism and fluorescence. For example, **Trop-DMA 4b** displays neither positive nor negative solvatochromism (Figure 1 a), which indicates that there are more than just solvating interactions between some of the studied solvents and organic dye **4b**. This dye is also fluorescent with Stokes shift of 107 nm in ethyl acetate (or $\approx 6272 \text{ cm}^{-1}$, Figure 1 b, the Stokes shift in acetonitrile is 76 nm or $\approx 6658 \text{ cm}^{-1}$, see page S20 in the Supporting Information).^[25]

Our newly developed organic dyes inherit some Lewis acidity, electrophilicity as well as oxidizing ability from the parent tropylium ion. During the synthesis of these dyes (4, Scheme 1), we noticed the susceptibility of their colors to pH change, suggesting that they might be useful as acid–base titrimetric indicators. We found that all organic dyes reported are pH-responsive but we only fully investigated two represen-



Figure 1. a) Solvatochromism of Trop-DMA 4b at 0.05 mm. b) Fluorescence of Trop-DMA 4b in EtOAc.

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tative members of this family, namely **Trop-26DIPA** (**4a**, discussed here in Figure 2) and **Trop-DEA** (**4c**, see pages S21–S28 in the Supporting Information). The initial experiment of



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Figure 2. pH-responsive organic dye Trop-26DIPA 4a. Top: Acid-base reaction; middle: pH titration profile; bottom: UV/Vis absorbance versus pH.

adding an excess amount of aqueous sodium hydroxide solution (1.0 M) to the purple solutions of **Trop-26DIPA 4a** in acetonitrile or water instantly decolorized those solutions. Subsequent addition of concentrated hydrochloric acid (10 M) resulted in the reformation of the purple solutions, suggesting that this is a reversible process. The color change of our tropylium dyes can be attributed to the nucleophilic addition of hydroxide anion to the tropylium scaffold at high pH, which resulted in the colorless cycloheptatrienyl alcohol adducts (**5 a**, presumably a mixture of regioisomers, in Figure 2), and the reformation of the aromatic tropylium moiety at low pH via protonation and subsequent dehydration to give the organic dye again.^[25]

Taking this result into a standard titration setup, a 0.2 mL of the stock solution (9.6 mM in acetonitrile) of **Trop-26DIPA 4a** was added to 25 mL of aqueous HCl solution (0.1 M), and it was titrated against an aqueous solution of NaOH (0.1 M) (resulting in the

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effective dye 4a concentration of 76 µм). Monitoring this acidbase titration by a pH probe and UV/Vis absorption spectroscopy, a purple-to-colorless change was visually observed at a pH 8.3 for Trop-26DIPA 4a (color change at pH 8.9 for Trop-**DEA 4 c**, see page S22 in the Supporting Information),^[25] which was consistent with the UV/Vis absorption spectrum of the solution (Figure 2 bottom). The reversed titration of NaOH by HCI using Trop-26DIPA 4a as indicator also observed the colorlessto-purple change at the same pH.^[25] Thus, the extraordinary chromophoric nature of these tropylium dyes allowed for observable color change in pH titrimetric conditions at indicator concentration of less than 40 μ M (concentration of 4a at equivalent point \approx 38 μ M). Further concentration-absorption studies revealed that the molar absorptivities of Trop-26DIPA 4a is $\approx 14 \times 10^3 \,\text{m}^{-1} \,\text{cm}^{-1}$ (see Supporting Information page S28),^[25] which is comparable to that of phenolphthalein.

As can be seen from the synthesis, the tropylium organic dyes were produced by the oxidative hydride abstraction reaction of cyclopheptatrienyl intermediates (Scheme 1). We were also able to perform the reversed hydride addition reaction to the tropylium moiety on these molecules to convert them back to cycloheptatriene derivatives. Thus, the reductive hydride addition reactions could be performed on all tropylium organic dyes using mild hydride donors such as sodium borohydride or hydrosilanes. Most interestingly, these organic dyes could survive multiple redox cycles, where they were subjected to sequential oxidative hydride abstraction by tropylium salt **2** and reductive hydride addition by NaBH₄.

A representative study with organic dye Trop-DEA 4c is depicted in Figure 3, in which it was cycled seven times through the redox hydride abstraction/addition process and still retained the original chromophoric capacity. Our quantitative UV/Vis absorption spectroscopic studies revealed that there were $\approx 5\%$ losses of absolute absorbance after each cycle, which can be attributed to losses of materials due to transfer and workup procedures. The pertinent sections from 450-750 nm of the UV/Vis absorption spectra (in acetonitrile) of the resulting unpurified compounds after each reaction are stacked together for comparison in Figure 3 (bottom). It is obvious that after each hydride addition reaction, the absorbance in the visible range decreased to zero, indicative of the cycloheptatriene form CHT-DEA 6c (colorless, which is presumably a mixture of regioisomers). Furthermore, after each hydride abstraction reaction it showed the characteristic absorbance peak at \approx 595 nm (purple) of the **Trop-DEA 4c** in acetonitrile. ¹H NMR of the crude product mixtures after each cycle also confirmed the interconversion of these two forms.^[25] Similar redox cycles and observations for Trop-26DIPA 4a can be found at page S29–S31 in the Supporting Information.^[25] These compounds and their analogues, thus, can potentially be used as redox-responsive organic dyes in the future.

Tropylium ion is known to coordinate to Lewis base such as phosphines.^[27] Despite being less electrophilic than the parent ion, the tropylium moiety in our organic dyes is still mildly Lewis acidic. These organic dyes were found to be able to coordinate to triphenylphosphine (Figure 4) to form substituted tropylium–triphenylphosphine complexes. A representative ex-



Figure 3. Top: Redox interconversion of Trop-DEA 4c to CHT-DEA 6c; bottom: pertinent UV/Vis spectra sections of the product after each redox cycle.

ample with organic dye **Trop-DMA 4b** is demonstrated in Figure 4. **Trop-DMA 4b** complexed with triphenylphosphine in a reversible process to form Ph_3P -CHT-DMA complexes 7b, which is presumably colorless. Low temperature favored the formation of the complexes while elevated temperature facilitated the thermolysis to the original **4b** dye and triphenylphosphine.

This equilibrium was monitored by variable temperature (VT) ³¹P NMR and UV/Vis absorption spectroscopy (Figure 4, middle and bottom, respectively). The ³¹P VT-NMR using a mixture of **Trop-DMA 4b** dye (20 mM) and triphenylphosphine (60 mM, signal at ≈ -5 to -7 ppm) in d₃-acetonitrile clearly showed two different types of **Ph₃P-CHT-DMA** complexes with ³¹P signals at -24 and -27 ppm (Figure 4, middle). These two signals kept their relative ratio consistent, which was also observable in ¹H NMR (see page S32 Supporting Information), but decreased in comparison to the triphenylphosphine signal when the temperature increased from 0°C to 45°C. At 0°C, it seemed that **Trop-DMA 4b** was completely converted to **Ph₃P-CHT-DMA 7b**, as evidenced by the colorless solution as well as ³¹P signal integration (spectrum 1, T=0°C).

Similarly, the VT-UV/Vis absorption spectroscopy (Figure 4 bottom) showed a clear intensification to the absorption peak at 567 nm (characteristic for organic dye **Trop-DMA 4b**) when the temperature increase from 10° C to 70° C. Since we used a 1:1 ratio of Ph₃P and **Trop-DMA 4b** and could only operate our apparatus within the $10-70^{\circ}$ C range, it was not possible to obtain the complete formation of the complexes **7b** or the complete dissociation to triphenylphosphine and organic dye **4b**. This VT-UV/Vis study, however, confirmed the complexation equilibrium and hints that we can potentially use organic dye **4b** and its analogues for applications in phosphine sensing and colorimetric analysis of chemical reactions, which

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Figure 4. Ph₃P-responsive organic dye **Trop-DMA 4b**. Top: Chemical reaction and color change; middle: ³¹P VT-NMR with Ph₃P:**4b**=3:1 ratio in CD₃CN; bottom: VT-UV/Vis absorption spectra with Ph₃P:**4b**=1:1 ratio in MeCN.

employ phosphines as organometallic ligands, stoichiometric reagents or catalysts.

Based on our previous works^[22b-d] and recent findings from Pöthig and co-workers on crystallographic data of tropylium salts,^[28] we believe that the tropylium moiety has different affinities to counterions, especially in the halide series. The ionic character of tropylium halide was observed to increase from chloride salt to bromide salt. It is of significant interest to explore the photo-physicochemical properties of our tropylium organic dyes in the presence of different halide anions.

In a preliminary study, compound **Trop-DMA 4b** (0.025 mM in acetonitrile), as a representative member of our tropylium organic dye family, was mixed and left to equilibrate with three equivalents of tetrabutylammonium halide (TBAX, 0.075 mM in acetonitrile) with the halide changing from F- to Cl- to Br- to I-. Interestingly while chloride (TBAC), bromide (TBAB) and iodide (TBAI) did not affect the absorbance of the organic dye to any noticeable extent based on UV/Vis absorption spectra (Figure 5, middle-left), the fluoride anion (TBAF) completely turned off the characteristic absorption peak at

 \approx 567 nm (Figure 5, middle-left and right). The **Trop-DMA 4b** dye turned colorless immediately upon the addition of TBAF (3 equiv) and it remained permanently so. The resulting solution was also luminescent under long-wavelength UV irradiation (365 nm, Figure 5, top right). These phenomena were not observed for TBAC, TBAB or TBAI.

It should be noted here that the fluoride sensing activity of our dyes is not due to the typical deprotonation-protonation event^[29] but due to the formation of covalently bonded adducts. ¹H NMR comparative studies showed that the **Trop-DMA 4b** in 1:3 mixture with TBAC (or TBAB and TBAI) retained its characteristic set of signals for the ionic tropylium moiety (**8b**, Figure 5) while forming a mixture of covalently bonding cycloheptatrienyl fluoride adducts F-CHT-DMA **9b** (colorless but luminescent) in the presence of TBAF (see page S39 in the Supporting Information for ¹H NMR spectra). A simple concentration study revealed that fluoride anion severely reduced the absorbance even at 1:1 ratio to the tropylium organic dye **Trop-DMA 4b** (Figure 5, middle right).

To confirm that this fluoride ion responsivity was not linked to the water content in the highly hygroscopic TBAF, we employed the anhydrous tetrabutylammonium triphenyldifluorosilicate (TBAT) as the fluoride source. Gratifyingly, very similar results to TBAF were obtained. Thus, the titration of a solution of TBAT (0.025 mm in MeCN) to a solution of Trop-DMA 4b (0.025 mм in MeCN, purple) slowly turned off the absorption peak at 567 nm, which completed at 3 equivalents of TBAT (Figure 5, bottom left). Although the fluorine seemed to be attached to the cycloheptatriene framework in F-CHT-DMA 9b via covalent bond (see page S39 in the Supporting Information for ¹H NMR evidence), it is still quite labile as a titration of *tert*butyldimethylsilyl chloride into the previously formed solution of F-CHT-DMA 9b (colorless) reformed the tropylium-cation of Trop-DMA 4b dye (increasing absorbance at 567 nm, purple, Figure 5, bottom left).

Furthermore, addition of water to a pre-formed colorless solution of F-CHT-DMA 9b with TBAF or CsF as the fluoride source changed it to purple color as well as regained the absorbance peak at 567 nm in its UV/Vis absorption spectra (Figure 5, bottom right). Clearly water has no role in the formation of F-CHT-DMA 9b or the sensitivity of Trop-DMA 4b dye to fluoride ion. The reformation of the purple color when water was added to F-CHT-DMA 9b solution can be attributed to the better solvation effect of the fluoride ion by water, which facilitates the fluoride cleavage from F-CHT-DMA 9b. In brief, Trop-DMA 4b dye is capable of detecting fluoride ion out of its halide family and the resulting fluorinated cycloheptatrienyl species (F-CHT-DMA 9b) can be converted back to its parent cation by treatment with TBDMS-Cl or simply adding water. Further investigations into selective fluoride sensing applications with Trop-DMA 4b dye and utilization of F-CHT-DMA 9b as an organic fluoride source are currently underway and will be reported shortly.

Structural optimizations and TD-DFT calculations of HOMO– LUMO transitions were conducted at CAM-B3LYP/6-31G(d) level of theory on organic dyes 4a'' and 4b'' (Figure 6). They exhibit symmetry-allowed HOMO \rightarrow LUMO transitions with high



Figure 5. Top-left: Anion exchange of **Trop-DMA 4b** with TBAX; top-right: decolorization and fluorescence of **4b** in the presence of fluoride; middle-left: UV/V is absorption spectra of **4b** versus TBAX (1:3); middle-right: UV/V is absorption spectra of **4b** versus TBAF (1:3, 1:1 and pure form); bottom-left: UV/V is absorption spectra of the titration of **4b** with TBAT then TBDMS-CI; bottom-right: UV/V is absorption spectra of the addition of water to **F-CHT-DMA 9b**.

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oscillator strengths of 0.8553 and 0.7385, respectively. In both compounds, the HOMOs are localized on the aniline rings while the LUMOs are localized on the tropylium moieties. Thus, the HOMO \rightarrow LUMO transitions in these organic dyes correspond to the intramolecular charge transfer from the aniline (push) to the tropylium (pull) moiety. Presumably due to this property, **4a**" and **4b**" (as well as the other dyes in this family, see pages S12–S16 in the Supporting Information) exhibit interesting solvatochromism in aqueous and organic solutions.

In conclusion, we have developed a family of novel cationic organic dyes using the unsubstituted tropylium ion as an electron-withdrawing chromophore. These bench-stable and water-soluble organic dyes can be synthesized from readily available synthetic precursors in practical one-pot chemical process. They exhibit interesting physicochemical properties such as solvatochromism, pH-sensitivity, redox-responsivity Lewis base and fluoride anion sensitivity. Further studies to develop these organic dye systems into advanced functional molecules for sensing applications are ongoing in our group and will be reported in due course.

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Figure 6. Molecular orbitals and relevant vertical excitations calculated by CAM-B3LYP/6-31G(d) method for the cations of 4a and 4b.

Conflict of interest

The authors declare no conflict of interest.

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COMMUNICATION

Push-Pull Systems

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Stimuli-Responsive Organic Dyes with Tropylium Chromophore



The development of a family of novel cationic organic dyes using the unsubstituted tropylium ion as chromophore is reported. They exhibit interesting physicochemical properties such as solvatochromism, pH-sensitivity, redox-responsivity Lewis base and fluoride anion sensitivity.